

# PATENT ABSTRACTS OF JAPAN

(11) Publication number : **10-100353**

(43) Date of publication of application : **21.04.1998**

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(51) Int.CI. **B32B 27/36**  
**B32B 23/08**

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## **(54) BIODEGRADABLE LAMINATED FILM**

### **(57) Abstract:**

**PROBLEM TO BE SOLVED:** To provide a biodegradable laminated film having biodegradability and excellent in sealability and transparency by providing a non-stretched film containing a polylactic acid type polymer and other biodegradable aliphatic polyester to one surface of a stretched film based on a polylactic acid type polymer.

**SOLUTION:** A non-stretched film to be used contains a polylactic acid type polymer and biodegradable aliphatic polyester different therefrom. It is pref. that the m.p. Tm of a stretched film composed of polylactic acid type polymer or a compsn. based thereof is 100°C or more. Aliphatic polyester different from polylactic acid is one having an alkylene-ester bond as a fundamental skeleton and a urethane bond, an amide bond or an ether bond can be introduced within a range not substantially exerting effect on biodegradability. Especially, an isocyanate compd. is used and a urethane bond can be introduced into the main chain thereof to jump up the mol.wt. thereof.

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### **LEGAL STATUS**

[Date of request for examination] **27.08.1997**

[Date of sending the examiner's decision of rejection]

[Kind of final disposal of application other than the examiner's decision of rejection or application converted registration]

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DETAILED DESCRIPTION  
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## [Detailed Description of the Invention]

[0001]

[Field of the Invention] It decomposes in natural environment and this invention relates to the biodegradability laminated film excellent in heat-sealing nature and transparency.

[0002]

[A Prior art and the technical problem which invention tends to solve] The general packing-material application which made the snack confectionery bag the typical example is begun, and the plastic film which was excellent in broad applications, such as agricultural materials, building materials, and biomedical materials, at transparency and heat-sealing nature is demanded.

[0003] Transparency is usually expressed by light transmission. Since the thing which has high permeability is excellent in transparency and contents can see it from an outside, it is used being fond as wrapping.

[0004] In case the so-called "heat sealing" of the film excellent in heat-sealing nature which sticks a film comrade by heat and the pressure, or is pasted up using a heating bar, a hot plate or a heating roller, etc. is carried out, it points to a film with the wide temperature requirement obtained by being stabilized in the bond strength for which it asks. That is, the film excellent in heat-sealing nature can obtain various kinds of film processing products simple by heat sealing.

[0005] On the other hand, when it is rejected from the rise about an environmental problem in natural environment to a plastic working article at large in recent years, the plastic which does not have an adverse effect on the natural environment which decomposes and disappears with time is called for.

[0006] However, the conventional plastic film product was stable over the long period of time in natural environment, and moreover, since relative bulk density was small, the trouble of having promoted the ephemeralization of a trash reclaimed ground or spoiling a natural scene and the living environment of wild nature animals and plants was pointed out.

[0007] Then, biodegradability plastic material attracts attention today. Biodegradable plastics are the inside of soil, and underwater, breaking and decomposition advance gradually according to hydrolysis or biodegradation, and becoming a harmless decomposition product according to an operation of a microorganism eventually is known.

[0008] The biodegradable plastic by which current and utilization are considered is divided roughly into aliphatic series polyester, Denaturation PVA (polyvinyl alcohol), a cellulose ester compound, a starch modification object, and these blend object.

[0009] However, in the biodegradable plastic mentioned above, heat-sealing nature and transparency equivalent to the polyethylene used conventionally, polypropylene, polyethylene terephthalate, etc. cannot be acquired.

[0010] Then, the object of this invention is to offer the biodegradability laminated film excellent in heat-sealing nature and transparency, having biodegradability.

[0011]

[Means for Solving the Problem] The summary of this invention is a biodegradability laminated film characterized by preparing the unstretched

film containing the biodegradability aliphatic series polyester with which a polylactic acid system polymer differs from a polylactic acid system polymer at one [ at least ] oriented film side which consists of a constituent which makes a principal component a polylactic acid system polymer or this. The biodegradability laminated film according to claim 1 of the melting point of said oriented film characterized by being higher than the melting point of said unstretched film is desirable. The summary of different this invention is a biodegradability laminated film characterized by preparing the unstretched film containing the biodegradability aliphatic series polyester with which a polylactic acid system polymer differs from a polylactic acid system polymer at one [ at least ] biodegradability cellulose film side.

[0012]

[Embodiment of the Invention] The polylactic acid system polymers used for this invention are the copolymers of polylactic acid or a lactic acid, and other hydroxycarboxylic acid, or these constituents, and can mix other polymeric materials in the range which does not check the effectiveness of this invention. Moreover, it is also possible to add additives, such as a plasticizer, lubricant, an inorganic filler, and an ultraviolet ray absorbent, and a modifier in order to adjust the physical properties and workability of a film.

[0013] L-lactic acid and D-lactic acid are mentioned as a lactic acid, and a glycolic acid, 3-hydroxybutyric acid, 4-hydroxybutyrate, a 3-hydroxy valeric acid, a 4-hydroxy valeric acid, a 6-hydroxy caproic acid, etc. are typically mentioned as hydroxycarboxylic acid.

[0014] The polymerization method is possible also for adopting well-known approaches, such as condensation-polymerization nature and a ring-opening-polymerization method, and may use a small amount of chain elongation agent, for example, a diisocyanate compound, a diepoxy compound, an acid anhydride, acid chloride, etc. for the purpose of molecular-weight buildup further. If the range of 60,000 to 1000 and 000 is desirable and turns around this range the bottom as weight average molecular weight of a polymer, practical use physical properties will produce a hardly discovered problem. Moreover, in turning a top, melt viscosity becomes high too much and is inferior to fabricating-operation nature.

[0015] For extending a polylactic acid system film, roll type or tenter-type a flat drawing machine, a tubular type drawing machine, etc. are used. Drawing temperature chooses draw magnification from the glass transition temperature of a polylactic acid system polymer within the limits of crystallization temperature, taking into consideration the amount of preferred orientation of a film within the limits of 6 or less times to at least 1 shaft orientations. The polylactic acid system film which has crystallinity is used and a film is heat-treated several seconds or more by within the limits from the crystallization temperature of the film after a drawing to the melting point to suppress a heat shrink.

[0016] It is desirable that the melting point  $T_m$  of the oriented film which consists of a constituent which makes a principal component a polylactic acid system polymer or this is 100 degrees C or more. At less than 100 degrees C, thermal resistance falls and  $T_m$  tends to cause a wrinkling etc. in fabricating etc. Moreover,  $T_m$  of a Pori L-lactic acid gay polymer is 195 degrees C, and  $T_m$  falls as copolymerization components, such as D-lactic acid, a glycolic acid, and a 6-hydroxy caproic acid, increase. For this reason,  $T_m(s)$  of the oriented film mentioned above on the actual target are 100 degrees C or more and 195 degrees C or less.

[0017] The unstretched film used by this invention contains different biodegradability aliphatic series polyester from a polylactic acid system polymer and a polylactic acid system polymer. A polylactic acid system polymer can use the same polylactic acid system polymer as what was mentioned above.

[0018] On the other hand, different aliphatic series polyester from polylactic acid cannot have alkylene and an ester bond as a basic frame, and can also introduce a urethane bond, amide association, ether linkage, etc. in the range which does not have real effect on biodegradability. Especially, using an isocyanate compound, a urethane bond can be introduced into a principal chain and molecular weight can be jumped up.

[0019] The compound shown in the generalization 1 obtained by specifically condensing aliphatic series diol and aliphatic series dicarboxylic acid is mentioned.

[0020]

[Formula 1]

(The inside R1 and R2 of a formula is the alkylene group, cyclo ring machine, or cyclo alkylene group of carbon numbers 2-10.) Moreover, n is polymerization degree required to become number average molecular weight 10,000-150,000. Amide association, a urethane bond, carbonate association, or alpha-hydroxycarboxylic acid may be contained in addition to this basic structure.

As aliphatic series diol, ethylene glycol, 1,4-butanediol and 1, and 4-cyclohexane dimethanol etc. is mentioned, and a succinic acid, an adipic acid, a suberic acid, a sebacic acid, dodecane diacid, etc. are typically raised as aliphatic series dicarboxylic acid. After choosing one or more kinds from these, respectively and carrying out a condensation polymerization, the polymer which jumped up weight average molecular weight or more to 50,000 with the isocyanate compound if needed can have the usually same basic physical properties as 60-110-degree C Tm and polyethylene, and can use them for this invention preferably.

[0021] Moreover, a series of aliphatic series polyester which carried out ring opening polymerization of the annular lactone using the organic metal catalyst is mentioned. As a monomer, epsilon-caprolactone, delta-valerolactone, a beta-methyl-delta-valerolactone, beta propiolactone, PIBARO lactone, beta-butyrolactone, gamma-butyrolactone, etc. are mentioned typically, and a lactide and glycolide are mentioned further. Conditions are adjusted and a polymerization is carried out so that one or more kinds may be chosen from these and weight average molecular weight may become 30,000 or more. Although control of Tm is performed by selection of a monomer, it is usually 50-170 degrees C.

[0022] As other synthetic system aliphatic series polyester, a radical polymerization object with the 2-methylene -1 which is an annular ketene acetal, 3-dioxolane and 2-methylene -1, and 3-dioxepane etc. is mentioned. [the polymer of a cyclic anhydride, oxiranes for example, a succinic anhydride and ethyleneoxide, propione oxide, or allyl glycidyl ether, ethylene, ]

[0023] Moreover, the aliphatic series polyester a biosynthesis is carried out [polyester] by acetyl-coenzyme A (acetyl CoA) within biomasses including Alcaligenes YUTOROFASU is known. Although this aliphatic series polyester is mainly poly-beta-hydroxybutyric acid (Pori 3HB), in order to put the practical use property as plastics on \*\*, it is industrially advantageous to devise a fermentation process, to usually copolymerize a valeric-acid unit (HV), and to make it the copolymer of Pori (3 HB-co-3HV). Generally HV copolymerization ratio is 0 - 40%, and Tm is 130-165 degrees C in this range. 4HB may be copolymerized instead of HV, or long-chain hydroxy alkanoate may be copolymerized.

[0024] In the existing petroleum origin composition system polymer, although polyvinyl alcohol (PVA) is comparatively excellent in biodegradability, a PVA homopolymer has the too large cohesive force of a molecule, and since melting extrusion molding cannot be performed without the melting point, when film-izing, it receives the constraint on a fabricating operation. Then, ethylene can be copolymerized or the vinyl acetate unit which usually disappears at a saponification process can be made to be able to remain, and it can reform and use so that it may have about 50-150-degree C Tm. The constituent which distributed starch etc. based on such a PVA system polymer in order to raise biodegradability is the so-called denaturation PVA, and can use it for this invention.

[0025] The film which consists of a cellulose or its derivative, for example, the acetyl cellulose acetylated to extent holding cellophane or biodegradability, is raised, and the biodegradability cellulose film used by this invention can be obtained by the solvent cast method or the melting extrusion method.

[0026] The unstretched film containing different biodegradability aliphatic

series polyester from a polylactic acid system polymer and a polylactic acid system polymer is produced as follows. There is the approach of extruding in the approach of extruding both from a mouthpiece, after feeding a raw material into the same extruder, respectively, and producing a direct film, or a strand configuration, producing a pellet, and producing a film with an extruder again. It is better to choose the latter to mix homogeneity, although all must take into consideration lowering of the molecular weight by decomposition. After fully drying different aliphatic series polyester from a polylactic acid system polymer and a polylactic acid system polymer and removing moisture, it fuses with an extruder. Polylactic acid chooses melting extrusion temperature suitably in consideration of the rate of that the melting point changes and mixing of both by the presentation ratio of L-lactic acid structure and D-lactic-acid structure. An about 100-250-degree C temperature requirement is usually chosen.

[0027] As for the rate of mixing of different aliphatic series polyester from a polylactic acid system polymer and a polylactic acid system polymer, it is desirable to make it the range of 75:25-20:80 by the polymerization ratio. If the rate of a polylactic acid system polymer exceeds 75%, the film obtained will become a crack, \*\*\*\*\*\*, and the thing that becomes empty and that is hard to treat practically for the hardness originating in polylactic acid, and brittleness. On the other hand, transparency is inferior when the rate of a polylactic acid system polymer is less than 20%. Usually, light transmission becomes being 75% or more with a film with a high feeling of transparency preferably 65% or more.

[0028] In the biodegradability laminated film of this invention, the oriented film which consists of a constituent which makes a principal component a polylactic acid system polymer or this serves as supporters, and the unstretched film containing different biodegradability aliphatic series polyester from a polylactic acid system polymer and a polylactic acid system polymer serves as a heat-sealing layer.

[0029] As for the melting point of the supporters who are the oriented films mentioned above, it is desirable that it is higher than the melting point of the heat-sealing layer which is the unstretched film mentioned above. By making the melting point high, at the time of sealing, supporters fuse, Siwa etc. does not occur, and setting out of seal conditions becomes easy. It is that the melting point of an oriented film is higher than the melting point of an unstretched film 10 degrees C or more still more preferably.

[0030] The oriented film which serves as supporters has the melting point. Since heat setting cannot do the amorphous film which does not have the melting point, heat-resistant temperature will become below a glass transition point. With the amorphous film of a polylactic acid system polymer, heat-resistant temperature becomes 60 degrees C or less, and cannot use it as supporters.

[0031] In the biodegradability laminated film of this invention, a biodegradability cellulose film can be used as supporters. As mentioned above, cellophane, an acetyl-cellulose film, etc. are mentioned to a biodegradability cellulose film. The so-called heat-resistant temperature from which light transmission is 90% or more, and appearance change of foaming etc. produces these biodegradability cellulose films is 160 degrees C or more.

[0032] In order to obtain the laminated film of this invention, there are the approach of sticking a film with adhesives, an approach of carrying out thermocompression bonding of the two films in optimal temperature with a hot platen or a roll, an approach that while began to wind, and extrudes and coats a film with the ingredient which constitutes the film of another side.

[0033] Also in the approach mentioned above, the dry lamination or the wet lamination method for using adhesives is simple. As adhesives, a vinyl system, acrylic, a polyamide system, a polyester system, a rubber system, an urethane system, etc. are common. Furthermore, when also making adhesives into biodegradability, the urethane which uses protein, such as polysaccharide, such as starch, an amylose, and an amylopectin, and glia, gelatin, casein, a zein, a collagen, polypeptides, non-vulcanized natural rubber or aliphatic series polyester, and aliphatic series polyester as a principal component is desirable.

[0034]

[Example] Hereafter, although an example is explained, this invention is not limited to this.

[0035] The monolayer which might be mentioned later or the light transmission of a laminated film, and heat-sealing nature were measured as follows.

[0036] (1) Light transmission JIS It measured based on K7105. Excelling in transparency is shown, so that a value is large.

[0037] (2) In the case of the simple substance film, in the case of the two-layer film, as it was, two sheets were arranged, the film test piece which cut down the heat-sealing nature film in 100mm and the size of 15mm of cross direction at the longitudinal direction was piled up so that sealing layers might face, and one end was heat sealed to 10mm width of face at right angles to a longitudinal direction. A sealing surface is set to 15mmx10mm. Using the metal heating bar with a width of face of 10mm in which temperature control is possible on a seal, it presupposed that it is fixed with pressure 1.0 kgf/cm<sup>2</sup>, and seal time amount 3 seconds, the temperature of a heating bar was changed, and seal nature was evaluated. in order [ in addition, ] to stop the welding to the heating bar of a film as much as possible -- the heat transfer side of a heating bar -- the product made from Teflon -- the tape which consists of the ground is stuck. Assessment investigated appearance change and reinforcement of a seal part.

[0038] Reinforcement extended each sample and asked for the maximum reinforcement which the part which carried out [ the part ] the chuck to the tension tester and carried out the seal to it exfoliates or fractures. The reinforcement per width of face of 15mm (kgf / 15mm) showed seal reinforcement. The tension test was performed by 80mm and speed-of-testing 100 mm/min between chucks using Oriental energy machine Tensilon 2 Mold machine.

[0039] Lacty (Shimadzu Make) which consists of [example 1 of experiment] polylactic acid was extruded from the T die at 220 degrees C with 60mmphi single screw extruder, it quenched with the casting roll, and the non-extended sheet with a thickness of about 140 micrometers was obtained.

[0040] It continued, it roll-extended 2.3 times at 75 degrees C, and ranked second to a longitudinal direction at them at them, and it extended by the tenter crosswise and this non-extended sheet was extended 2.5 times at 70 degrees C. Then, it heat-treated in temperature [ of 120 degrees C ], and processing-time 25 seconds in the heat treatment zone of a tenter, and the 20-micrometer biaxial orientation drawing polylactic acid film was obtained.

[0041] Moreover, after carrying out mixed fusion of the Bionolle #1001 (Showa High Polymer Co., Ltd. make) which consists of a condensation product of the Lacty (Shimadzu Make), the 1,4-butanediol, and the succinic acid which consist of polylactic acid at a rate of 70:30 using the 25mmphi said direction small biaxial extruder, it extruded in the strand configuration at about 200 degrees C, and the pellet was produced. Next, the unstretched film of 40-micrometer thickness was produced at the casting humidity of 52 degrees C using the 30mmphi small single screw extruder.

[0042] Two kinds of obtained films were stuck. One side of both films was pasted up on lamination by the dry lamination method, after performing corona surface treatment for energy 24 W/m<sup>2</sup>/beforehand. That is, polyurethane system solvent type adhesive was applied to homogeneity in the processing side of a polylactic acid biaxial oriented film so that it might be about set to 1 micrometer, another film was piled up so that a processing side might suit adhesives, and it was stuck by pressure with the roller. It let it pass for several seconds to the drying furnace continuously set up at 70 degrees C, dried to it, and aged for three days at 40 more degrees C.

[0043] The biodegradability laminated film was obtained like the example 1 of an experiment except having used Bionolle #3001 (Showa High Polymer Co., Ltd. make) which is the co-condensation polymerization object of 1,4-butanediol, and the succinic acid/adipic acid as biodegradability aliphatic series polyester other than the polylactic acid used for the [example 2 of experiment] unstretched film.

[0044] The biodegradability laminated film was obtained like the example 2 of an experiment except having set to 70:30 to 50:50 and 25:75 the presentation ratio of the polylactic acid system polymer used for the [examples 3 and 4 of

experiment] unstretched film, and biodegradability aliphatic series polyester other than polylactic acid.

[0045] The biodegradability laminated film was obtained like the example 3 of an experiment except having used the plaque cel H7 (Daicel Chemical Industries, Ltd. make) which consists of a poly caprolactone as biodegradability aliphatic series polyester other than the polylactic acid used for the [example 5 of experiment] unstretched film.

[0046] after carrying out melting push appearance of Lacty (Shimadzu Make) which consists of [example 6 of experiment] polylactic acid using a 30mmphi small single screw extruder, it took over quenching by KYATINGUDORAMU made into the skin temperature of 57 degrees C, and the film with a thickness of 40 micrometers was produced.

[0047] The monolayer film of 40-micrometer thickness was obtained for Bionolle #1001 (Showa High Polymer Co., Ltd. make) which consists of a condensation product of [example 7 of experiment] 1,4-butanediol, and a succinic acid at the casting temperature of 52 degrees C using 30mmphi and a small single screw extruder.

[0048] The unstretched film obtained in the example 3 of the [example 8 of experiment] experiment was used as it was.

[0049] The film obtained in the oriented film and the example 7 of an experiment in the example 1 of the [example 9 of experiment] experiment was stuck by the same approach as the example 1 of an experiment.

[0050] Transparency cellophane with a [example 10 of experiment] thickness of 21 micrometers and the unstretched film [ finishing / corona surface treatment ] obtained in the example 2 of an experiment were stuck by the same approach as the example 1 of an experiment.

[0051] Transparency cellophane with a [example 11 of experiment] thickness of 21 micrometers and the unstretched film which carried out corona surface treatment of the film obtained in the example 7 of an experiment were stuck by the same approach as the example 1 of an experiment.

[0052] Light transmission and heat-sealing nature were investigated about the sample obtained in the examples 1-11 of an experiment mentioned above. the result of the examples 1-5 of an experiment -- a table 1 -- said -- the result of 6-9 -- a table 2 -- said -- the result to 10-11 is shown in a table 3. In addition, four steps of O0\*\*x showed comprehensive assessment. O - \*\* -- the practical use range -- it is -- x -- practical use -- a thing out of range is shown. For the sample of the examples 1-5 of an experiment, the example of this invention and the examples 6-9 of an experiment are [ the example of this invention and the example 11 of an experiment of the example of a comparison and the example 10 of an experiment ] examples of a comparison.

[0053]

[A table 1]

[A table 2]

[A table 3]

As for both the laminated films of this invention which consists of an unstretched film containing the oriented film which consists of a constituent which makes a principal component a polylactic acid system polymer or this, and different biodegradation aliphatic series polyester from a polylactic acid system polymer and a polylactic acid system polymer, light transmission and heat-sealing nature have fallen within the practical use range so that clearly from a table 1. On the other hand, in the example of a comparison shown in a table 2, light transmission or heat-sealing nature has deteriorated. Moreover, as shown in a table 3, even if it uses a biodegradability cellulose film for supporters, it excels in the laminated film of the configuration of this invention at light transmission and heat-sealing nature.

[0054]

[Effect of the Invention] As mentioned above, since the laminated film of this invention has the transparency and heat-sealing nature which were excellent, using the ingredient which has biodegradability as explained, it is suitable for manufacture of an environment-friendly bag ingredient etc.

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**CLAIMS**

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**[Claim(s)]**

[Claim 1] The biodegradability laminated film characterized by preparing the unstretched film containing different biodegradability aliphatic series polyester from a polylactic acid system polymer and a polylactic acid system polymer in one [ at least ] oriented film side which consists of a constituent which makes a principal component a polylactic acid system polymer or this.

[Claim 2] The melting point of said oriented film is a biodegradability laminated film according to claim 1 characterized by being higher than the melting point of said unstretched film.

[Claim 3] The biodegradability laminated film characterized by preparing the unstretched film containing different biodegradability aliphatic series polyester from a polylactic acid system polymer and a polylactic acid system polymer in one [ at least ] biodegradability cellulose film side.

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[Translation done.]